

LIQUEFACTION OF WATER PRETREATED COALS

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INTRODUCTION

Water pretreatment of coal has been studied previously as a means to increase the yields of liquid products from extraction (1-5), pyrolysis (3-6), or liquefaction (7,8) of coal. However, the mechanisms of this process and the applications to coals of a wide range of ranks are still a subject of considerable debate. The benefit of water pretreatment on increasing yields from direct liquefaction of coal has not been clearly demonstrated, although effects on the composition and molecular weight distribution have been observed (7,8). The goals of this study are to gain an understanding of the chemistry of water or steam coal pretreatments and to assess the importance of such pretreatments on subsequent coal liquefaction.

EXPERIMENTAL

Sample Selection - The selection of coal samples was made from the Argonne Premium Sample Bank. Since pretreatment is potentially most useful for lower rank coals which are subject to retrograde reactions, the coals used were the Zap Lignite, the Wyodak subbituminous and the Illinois No. 6 bituminous. Selected experiments were also done with the Pittsburgh Seam bituminous coal from the same sample bank.

Steam/Water Pretreatment Experiments - A new reactor system was designed to carry out high pressure (up to 6000 psig), high temperature (up to ~ 400°C) steam or water pretreatment of coal in a closed bomb (20 ml) reactor. After 1-3 g coal is fed into the bomb and the reactor head is screwed on to get a gas tight seal, the system is purged with N₂ or evacuated, the high temperature, high pressure valve on the reactor base is closed, and the water is injected directly into the coal through the capillary tube with a ~ 0.1-1.0 ml/min rate. Deaerated and deionized water is used throughout the reaction.

Simultaneously with the water injection, the reactor is immersed into the fluidized sand bath held at the required temperature. The pressure is measured in the water feed capillary tubing directly after the pump. The amount of water pumped in and the temperature determines whether steam and/or water pretreatment is done. The results described in the current paper are for pretreatment with subcritical water at 350°C, 4000 psig and pretreatment times from 10 to 1000 minutes.

After the reaction, the bomb is quickly quenched with water, flooded with up to 300-600 psig N₂ and depressurized with a 0.8 liter previously evacuated sampling tank. The yields of product gases, e.g., H₂, CO₂, CO, CH₄, C₂H₆, C₂H₄, C₂H₂, and H₂S are determined by GC. After opening

the reactor, the pretreated coal is taken out of the reactor by washing it with deionized water and filtering under an N_2 atmosphere. N_2 is passed through the coal sample for about an hour to obtain a sample with approximately the same moisture content as the starting coal sample. In addition to the reactor, an N_2 purged glove box was also constructed to facilitate all the product work up in an oxygen-free environment.

Product Analyses - The residues from the water pretreatment experiments with the four coals were subjected to analysis by programmed pyrolysis (TG-FTIR), solvent extraction, FT-IR, SEM/x-ray analysis and liquefaction experiments in a donor solvent. The liquefaction experiments were done with 0.5 g of coal residue and 3 g of solvent (dihydrophenanthrene) in a 20 ml agitated bomb reactor for 30 min. at 400°C.

RESULTS

Experiments with a Range of Coals - Selected results for the characterization of the residues by TG-FTIR, solvent extraction with pyridine, and liquefaction experiments in a donor solvent are summarized in Figs. 1-3. The results for pyrolysis tar yields (Figs. 1a, 2a, 3a) show a sharp increase at short pretreatment times with a gradual decrease at longer times when compared to the raw coal. The oxygenated gases, CO, CO_2 and H_2O (data not shown) decline with increasing pretreatment time, except for an initial increase in CO. Conversely, the amount of CH_4 from pyrolysis has the opposite trend.

The set of data on pyridine extractables is less complete but indicates that, for the three coals, the yield increases at relatively short pretreatment times (by as much as a factor of two) and gradually declines at longer pretreatment times (see Figs. 1e, 2e, 3e), thus following the same general trend as the tar yield. The larger set of data for the Illinois coal is quite clear with regard to this trend. In the case of the Illinois coal, pretreatment for 20 minutes resulted in a more than doubling of the % DAF pyridine extractables (81 vs. 36%). The results were generally lower when an ampoule of Illinois coal was used which was not freshly opened (compare open circles and solid circles in Figure 3). The results to date indicate that of the four coals examined (Zap, Wyodak, Illinois, Pittsburgh), the Illinois coal is the most sensitive to coal freshness. For the Pittsburgh coal, the pyridine extractables increase slowly with increasing pretreatment time.

The liquefaction results for the two low rank coals (Zap, Wyodak) indicated significant reductions at short pretreatment times, particularly for the Zap lignite, in the yields of toluene and pyridine solubles (see Figs. 1f and 2f). The liquefaction yields for the low rank coals improved at longer pretreatment times but were generally not as high as for the untreated coal. Conversely, improved or similar yields of oils and toluene solubles are observed for selected pretreatment experiments with Illinois coal. However, these results could not be reproduced consistently with Illinois coal. It appeared that the results were sensitive to the "freshness" of the coal. For ampoules which were just opened, the yields of soluble products from the pretreated coals were lower than for samples which had been opened days or weeks earlier and stored in a nitrogen purged glove box. A likely explanation is that the solvent is forming adducts with the water pretreated samples. This conclusion is supported by the observation of negative oil yields, since the oil yields are determined by difference. The very fresh Illinois samples appear to be the most reactive toward solvent adduction. The differences between the fresh and "aged" Illinois samples is also evident by comparing the yields of pyrolysis gases and pyridine extractables in Fig. 3. This same phenomenon may explain why the liquefaction yields for the pretreated Zap and Wyodak coals go through a minimum at short pretreatment times, and are generally less than for the raw coals.

This hypothesis was tested by doing mild oxidation experiments on raw and pretreated Illinois and Zap coals, as discussed below.

Mild Oxidation Experiments - The samples generated in the mild oxidation studies were subjected to characterization by liquefaction in donor solvent (30 min., 400°C in dihydrophenanthrene). The results for toluene solubles and oils for the mild oxidation experiments and reference experiments are summarized in Table 1. This table only includes data for freshly opened ampoules in the case of Illinois coal. Experiment #80 indicates that mild oxidation of a

TABLE I - SUMMARY OF LIQUEFACTION EXPERIMENTS ON ILLINOIS AND ZAP COALS

Coal Type	Run No.	Treatment	Liquefaction Yields DAF %	
			Toluene Solubles	Oils
Ill. #6		---	42 to 48	14 to 17
		pretr.	11 to 40	(-12) to 40
	80	pretr. + H ₂ O ₂ ^(b)	64	19
	84	H ₂ O ₂ ^(a) + pretr.	48	7
	88	H ₂ O ₂ ^(b) + pretr.	62	19
	91	Fe ⁰ + (c)	49	7
	85	H ₂ O ₂ ^(b)	53	12
	93	H ₂ O ₂ ^(b) + H ₂ S*	90	34
Zap		---	26 to 36	12 to 14
		pretr.	18 to 21	12 to 15
	82	pret. + H ₂ O ₂ ^(b)	30	14

Notes: 150 ML solution, 5 gr. coal: (a) 0.003 M (b) 0.5 M (c) 1 M

All water pretreatments were done at 350°C, 4000 psig for either 20 minutes (#80, #82) or 60 minutes (#84, #88) pretreatment time.

* Liquefaction was done in the presence of 80 psig H₂S.

water pretreated Illinois coal gives an increased yield of toluene solubles and oils from liquefaction of the residue and that the values are generally higher than from liquefaction of the raw coal. Similar results are observed for mild oxidation of a water pretreatment residue from Zap lignite (see experiment #82 in Table 1). These results are consistent with the hypothesis that ortho dihydroxy functionalities created by water pretreatment are responsible for the retrogressive solvent incorporation reactions which artificially reduce the liquefaction yields. This conclusion is based on the assumption that the mild oxidation will remove the dihydroxy functionalities. Additional experiments were done with Illinois coal (#84, #88) where the coal was oxidized prior to water pretreatment. This would serve to remove dihydroxy functionalities which are already

present in the coal and the phenolic groups that are precursors to the dihydroxy functionalities that are formed during water pretreatment. In this case, the toluene solubles and oil yields are also higher than for the coal that was only subjected to water pretreatment. It was also found that mild oxidation by itself (#85) or mild oxidation followed by liquefaction in the presence of H_2S (to restore catalytic activity of pyrite) also gave results that were equal or superior to the raw coal.

FT-IR Analyses of Water Pretreated Coals - Residues from water pretreatment of all four coals were subjected to analysis by quantitative FT-IR functional group analysis. The samples were chosen from a range of pretreatment times (20, 180, 300, 1080, 1200 minutes) at 350°C, 4000 psig. The quantitative results for aromatic hydrogen (H_{ar}), aliphatic hydrogen (H_{al}), hydroxyl hydrogen (H_{OH}) and ether oxygen (O_{ether}) are given in Fig. 4. For all of the coals, except Pittsburgh, pretreatment led to a monotonic decline in the oxygen content. This is consistent with previous work on water pretreatment (6-9) and with the idea that the process is similar to an accelerated aging of the coal.

A lot of attention has been paid to the effect of water or steam pretreatment on hydroxyl groups. For all four coals, the concentration of hydroxyl OH declined with increasing pretreatment time, except for a small initial increase with Zap. This is in agreement with the results of Khan et al. (9) but not with Brandes et al. (6). Brandes et al. (6) concluded that steam pretreatment significantly increased the number of hydroxyl groups. This conclusion was primarily based on the fact that mild O-alkylation of steam pretreated coal with labeled methyl iodide introduced twice the enrichment of ^{13}C when compared to the raw coal. Some IR data was also used to support this conclusion, using a diffuse reflectance technique which measures surface concentrations. It is possible that the loosening of the structure resulting from steam pretreatment makes the coal more reactive toward the O-alkylation procedure, and that the actual number of hydroxyl groups does not increase significantly. It is also possible that the concentration of OH groups increases on the surface of the water pretreated coals but not in the bulk. Of course, any comparison with previous work must consider the fact that the results in Fig. 4 are for samples produced in subcritical water and over a wide range of pretreatment times. Most of the previous studies (3-6,9) were done in subcritical steam at lower pressures (~1000 psig) and for relatively short times. Some additional work on resolving the -OH region of the spectrum indicated that the concentration of ortho dihydroxy functions does initially increase for all of the coals following water pretreatment.

The trends for hydrogen functional groups appeared to vary with coal type. For the two low rank coals (Zap, Wyodak), pretreatment increased the fraction of aromatic hydrogen, while for the two higher rank coals (Illinois, Pittsburgh), this fraction was decreased. The contrast between the behavior of the Zap and Illinois coals is especially striking in this regard. For the two low rank coals, the amount of aliphatic hydrogen (H_{al}) goes through a maximum with increasing pretreatment time, while for the two higher rank coals, H_{al} declines steadily.

DISCUSSION

The increase in pyridine extractables and tar yields is consistent with literature observations (4,6,9). The tar yields and pyridine solubles yields show a maximum with increasing pretreatment time (except for the Pittsburgh coal) which indicates the onset of retrograde reactions as pretreatment proceeds (10). Conversely, the yields of toluene solubles (TS) from liquefaction are

at a minimum where pyrolysis tar yields are at maximum, which is contrary to previous studies on liquefaction (11) and expectations. However, the individual experimental data around the minimum toluene solubles values were very dispersed, especially for the Illinois No. 6 coal.

Table 1 shows the liquefaction results of experiments with Illinois No. 6 coal in somewhat more detail. Since the oil fraction is measured by weight difference, the only explanation for negative values is that there was solvent incorporation into the toluene insoluble part of the coal matrix and that this depends on how fresh the coal was. In the case of the Illinois coal, an exposure of this particular coal to even very low oxygen concentrations prior to pretreatment apparently causes a very significant change in the pretreatment and subsequent liquefaction behavior. There are reports in the literature of the sensitivity of Illinois No. 6 coal to rapid oxidation at ambient temperatures (12,13). The problem of measuring the incorporated solvent calls for a proper separation of the solvent and solvent derivatives which is very difficult to do on a quantitative basis given the complex nature of the coal liquid.

A second approach, which we have taken, is to hypothesize a reaction scheme for that particular behavior which is in harmony with the experimental data and then to test it. Our hypothesis is that it is the phenoxy radical which reacts with water to form dihydroxy products, as illustrated in Fig. 5, and that the recombination of the dihydroxy and solvent radicals leads to solvent incorporation into the coal matrix, as illustrated in Fig. 6. However, dihydroxy compounds are not stable at such high temperatures and must therefore appear only as intermediate products leading to the "recovery" of the toluene solubles yields after prolonged pretreatment. An example of two decomposition routes for ortho dihydroxy benzenes is shown in Fig. 7.

Phenols are the most widespread components of coals and literature data show a decrease of total phenolic OH in the coal as well as increase of low molecular weight dihydroxy benzenes during water pretreatments (7,14). Our own FT-IR results support this picture as does the initial increase in pyrolytic CO formation (see below). Since phenoxy radicals are relatively stable due to resonance stabilization, they represent a high steady state concentration at elevated temperatures. As the number of condensed aromatic rings adjacent to the phenoxy radical increases, the stability increases and the reactivity decreases. This might be an explanation as to why the Pittsburgh coal behaves differently during water pretreatment than the lower rank coals.

Dihydroxy benzenes are prone to retrograde reactions (15) or decomposition. One type of decomposition may lead to CO evolution from the residue as shown in Fig. 7. Our experimental data show an initial increase in the pyrolytic CO evolution with a maximum in time corresponding to the minimum in the toluene solubles yield and the maximum in the tar yield (see Figs. 1-3). This is in contrast to a general decline in pyrolytic CO₂ and H₂O with increased pretreatment time and a corresponding reduction in organic oxygen content for the water pretreatment residues. There is a small amount of CO formation during pretreatment, but it is an intermediate product only.

McMillen and coworkers (15) found that, under liquefaction conditions, dihydroxy compounds readily couple with themselves or with the solvent (in their case, tetrahydroquinoline) and also form high molecular weight products, the amount of which increases in the presence of coal. The self coupling produces a diaryl cyclic ether molecule. This is consistent with our FT-IR data, (see Fig. 4) which show the ether group concentration reaching a maximum or declining slowly after relatively short hydrothermal treatment times, while the concentration of hydroxyl decreases steadily.

Our suggestion is that one of the principal reactions to cause solvent incorporation into the coal matrix under liquefaction conditions is the reaction of surface ortho dihydroxy functionalities with the solvent. A short hydrothermal treatment will enhance solvent incorporation due to the increased surface concentration of dihydroxies. Prolonged pretreatment will destroy these functionalities, as shown by Ross et al. (12), thus reducing solvent additions but introducing strong crosslinks and resulting in a decrease in liquefaction yields. A parallel process of depolymerization of the coal during hydrothermal treatment is compensating for this new crosslink formation, the final result being a slight increase or no increase of liquefaction yields relative to the untreated coal at long pretreatment times. The proposed mechanism is summarized in Fig. 8.

Since higher yields of toluene solubles and oils were obtained from samples of Illinois coal that were not freshly opened, or were treated with solutions of H_2O_2 our suggestion is that a mild oxidation substantially decreased solvent incorporation by removal of ortho dihydroxy functionalities or their precursors. This result suggests a possible way to avoid the detrimental effect of solvent incorporation and thus significantly increase liquefaction yields from water pretreated coals. Future work will involve additional experiments and literature work to test the hypothesis. The results will also be considered in light of the recent model compound studies of Siskin and Katritsky (16).

CONCLUSIONS

The conclusions can be summarized as follows:

1. The analysis of pyrolysis and pyridine extractables data from water pretreated Zap lignite and Wyodak subbituminous coal (reduction in CO_2 yield, maximum in tar yield, maximum in extractables, increase in CH_4 yield) shows a strong similarity of water pretreatment to an accelerated geological aging process. The results for the Illinois and Pittsburgh bituminous coals were similar, though less dramatic, except for the extractables yields.
2. The geological aging analogy is also consistent with results that were obtained in the literature on steam or water pretreatment, since it explains why the treatment is effective in increasing pyrolysis yields for low rank coals and is ineffective or reduces pyrolysis yields for high rank coals. However, there are certain trends, such as the fact that the CO yield appears to follow the tar yield (goes through a maximum along with the tar) which do not agree completely with this analogy.
3. The FT-IR data indicate a general reduction of oxygen groups during water pretreatment, including hydroxyl groups, although there is an initial increase in dihydroxy functionalities.
4. The results from liquefaction experiments on samples produced to date indicate only modest benefits in the best cases. The worst results are obtained at short pretreatment times where solvent incorporation into the coal is apparently reducing the observed yields of soluble products. For Illinois coal, the best results are obtained from "aged" samples, which appear to be less prone to the solvent adduction reactions.

5. The data are consistent with a mechanism in which water pretreatment increases the concentration of ortho dihydroxy species in the coal at short pretreatment times. Support is provided by FT-IR results and an initial increase in pyrolytic CO formation from the residue. These functions are believed to be responsible for the solvent incorporation reactions. They can be removed by increasing the pretreatment time or mild oxidation of the coal using H_2O_2 after water pretreatment.

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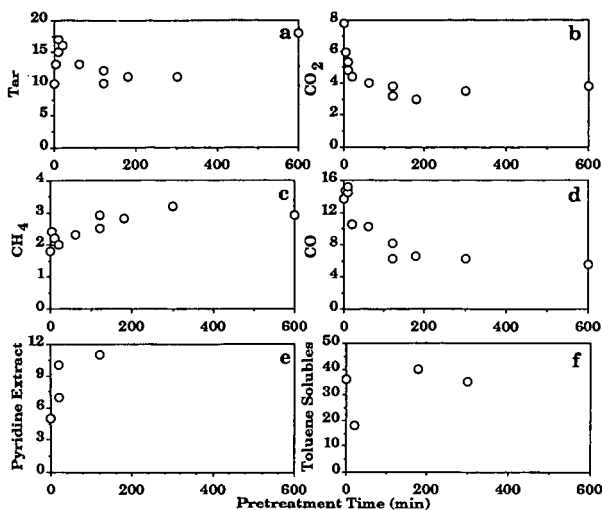


Figure 1. Results from Analysis of Zap Residues Produced by Water Pretreatment at 350°C, 4000 psig for a Range of Pretreatment Times. (a-d) Data on Pyrolysis Gas Yields from TG-FTIR Analysis; (e) Data for Extractables Yield Using Pyridine at Room Temperature; (f) Data for Toluene Solubles Yield from Donor Solvent Liquefaction. All Results are Given on a DAF Basis.

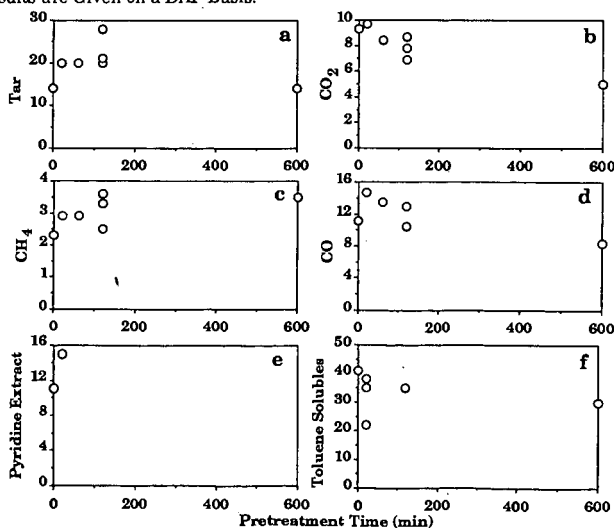


Figure 2. Results from Analysis of Wyodak Residues Produced by Water Pretreatment at 350°C, 4000 psig for a Range of Pretreatment Times. (a-d) Data on Pyrolysis Gas Yields from TG-FTIR Analysis; (e) Data for Extractables Yield Using Pyridine at Room Temperature; (f) Data for Toluene Solubles Yield from Donor Solvent Liquefaction. All Results are Given on a DAF Basis.

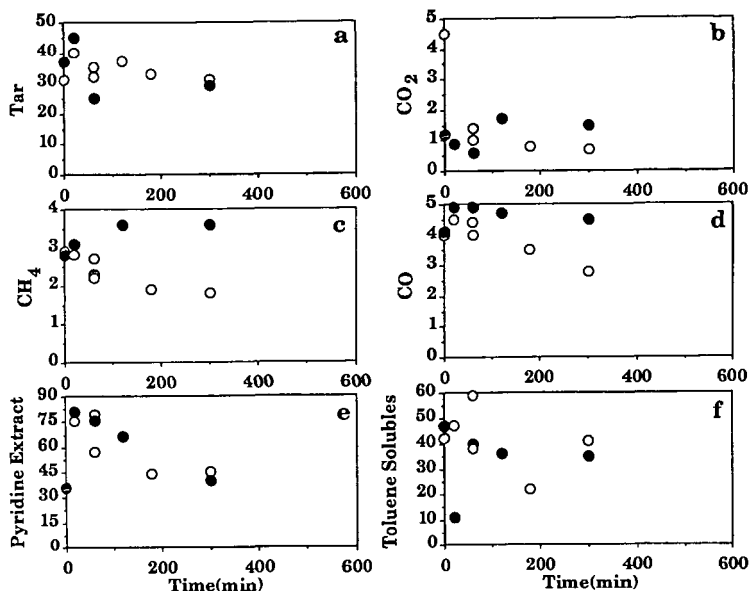


Figure 3. Results from Analysis of Illinois Residues Produced by Water Pretreatment at 350°C, 4000 psig for a Range of Pretreatment Times. (a-d) Data on Pyrolysis Gas Yields from TG-FTIR Analysis; (e) Data for Extractables Yield Using Pyridine at Room Temperature; (f) Data for Toluene Solubles Yield from Donor Solvent Liquefaction. All Results are Given on a DAF Basis. Solid Circles are for Freshly Opened Samples. Open Circles are for Samples which had been Previously Open.

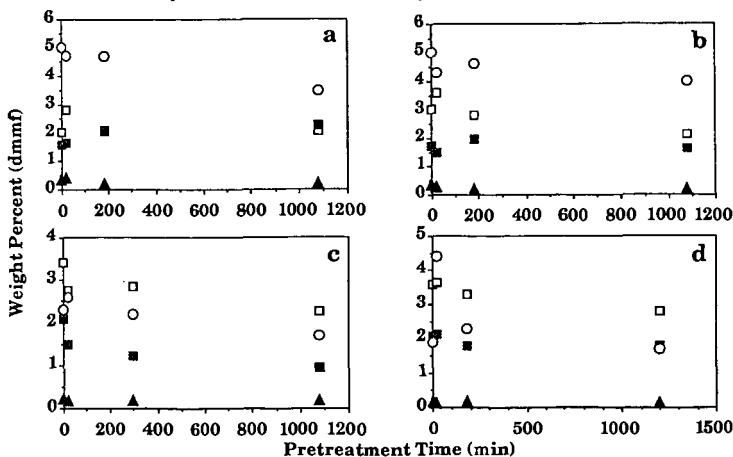


Figure 4. Results from FT-IR Analysis of Residues from Four Coals Produced by Water Pretreatment at 350°C, 4000 psig for a Range of Pretreatment Times. a) Zap; b) Wyodak; c) Illinois; d) Pittsburgh. □ - H_{al}; ■ - H_{ar}; ▲ - H_{oh}; ○ - O_{ether}.

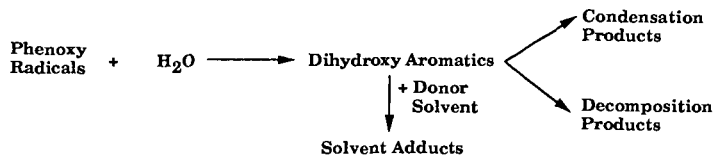
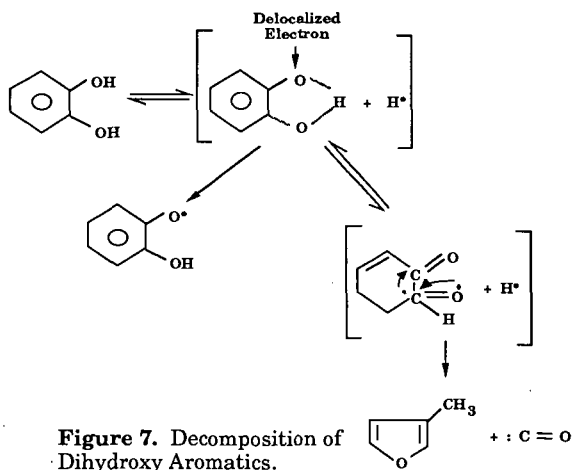
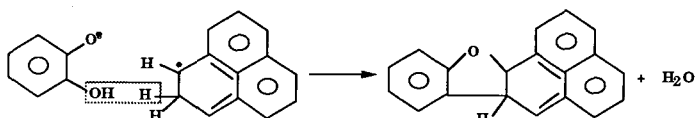
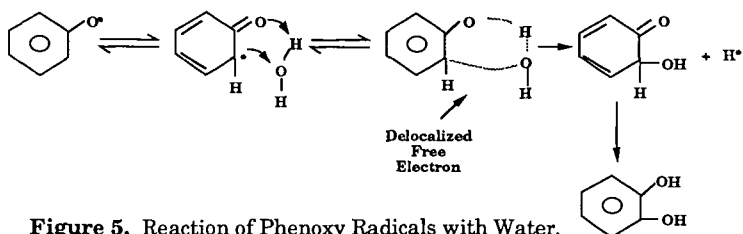


Figure 8. Proposed Mechanism for Water Pretreatment as it Impacts Liquefaction Yields.